PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference E-2366/04	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/IB2004/002960	International filing date *(day/month/year)* 10.09.2004	Priority date *(day/month/year)* 11.09.2003
International Patent Classification (IPC) or national classification and IPC C23C14/22		
Applicant EDISON S.P.A. at al.		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 5 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
28.09.2005	11.01.2006
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Patterson, A Telephone No. +31 70 340-3421

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IB2004/002960

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ ~~This report is based on~~ translations from ~~the original language into the following~~ language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1, 3-9	as originally filed
2	received on 28.09.2005 with letter of 28.09.2005
Claims, Numbers	
1-21	received on 28.09.2005 with letter of 28.09.2005
Drawings, Sheets	
1/2, 2/2	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-21
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-21
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (SEPARATE SHEET)

International application No.
PCT/IB2004/002960

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: DE 44 08 052 C1 (KERNFORSCHUNGSZENTRUM KARLSRUHE GMBH, 76133 KARLSRUHE, DE) 20 April 1995 (1995-04-20)
D2: DE 36 10 294 A1 (CANON K.K; CANON K.K., TOKIO/TOKYO, JP) 2 October 1986 (1986-10-02)
D3: GB-A-2 175 414 (CANON KABUSHIKI KAISHA) 26 November 1986 (1986-11-26)
D4: DATABASE WPI Section Ch, Week 199110 Derwent Publications Ltd., London, GB; Class M13, AN 1991-071293 XP002332491 & SU 1 554 986 A (AS UKR MATERIAL SCI) 7 April 1990 (1990-04-07)
D5: DATABASE WPI Section Ch, Week 198628 Derwent Publications Ltd., London, GB; Class A25, AN 1986-182274 XP002332492 & SU 1 199 295 A (BELGOROD PLASTICS WKS) 23 December 1985 (1985-12-23)
D6: DE 196 31 101 A1 (SIEMENS AG, 80333 MUENCHEN, DE) 5 February 1998 (1998-02-05)

D6, considered to represent the closest prior art, describes a method of depositing films of coating material and a corresponding apparatus in which precursors of the film material are evaporated onto the substrate in an evaporation area while, at the same time, a stream of oxidising gas is supplied.

The method and apparatus according to the independent claims 1 and 13, respectively, differ from this prior art disclosure in that a gas flow is supplied by ultrasonic expansion of the flow. The claimed subject-matter is therefore new in the sense of Article 33(2) PCT.

With respect to the closest prior art, the subject-matter of the independent claims solves the problem of assuring sufficient pressure of gas adjacent to the substrate (eg to oxidise the deposited film) without utilising a gas supply means which is located in close proximity

to the substrate. This solution is not suggested by any of the documents D1-D5, which of which teaches the use of an ultrasonic gas flow to transport fine particles, especially clusters. Therefore the claimed subject-matter involves an inventive step in the sense of Article 33(3) PCT.

Further, preferred embodiments are given by the dependent claims 2-12 and 14-21.

the serious drawback that, in order to ensure a significant increase in oxygen pressure, they entail maintaining the edges of the box at a very small distance from the surface of the film being grown (in the region of a tenth of a millimetre). It is consequently necessary to envisage not only an accurate initial adjustment of the position of the diffuser, but also a continuous and accurate control of the distance of the diffuser from the surface of the film being grown during deposition. To ensure effective operation of this type of devices, it is hence necessary to envisage complex systems of tightness and/or refined systems of mechanical positioning. In any case, there is not a fully satisfactory reliability of the process.

In deposition processes of different type, for example by spraying, cluster beam, powder or particles coating as described in DE-4408052-C1, DE-3610294-A1, GB2175414-A), it is known to suspend the deposition material in a ultrasonic gas flow.

DISCLOSURE OF INVENTION

A purpose of the present invention is to provide a method and an apparatus for deposition of films of coating materials, in particular for deposition of films of superconductive oxides and/or buffer layers in processes of fabrication of superconductive composite tapes, which will be free from the drawbacks of the known art referred to above. In particular, a purpose of the invention is to provide a method and an apparatus that will also enable continuous operation at high processing rates, ensuring an effective deposition and a high reliability and presenting at the same time a simple and economically advantageous embodiment.

In accordance with said purposes, the present invention relates to a method and an apparatus as defined in the annexed Claims 1 and 13, respectively.

The method and apparatus according to the invention enable a significant increase in the effective oxygen pressure to be achieved in the deposition area, so that said oxygen pressure is comparable to the one that can be obtained with available systems, but without any need for complex constructional and

CLAIMS

1. A method of deposition of films of coating materials on a substrate, in particular for deposition of films of superconductive oxides and/or buffer layers of superconductive composite tapes, comprising a step of deposition of a film (2) on the substrate (4) associated to a step of gas treatment *in situ*, in which a flow (13) of gas is sent towards a working surface (14) of the substrate (4) or of the film (2) growing on the substrate, the method being characterized in that said deposition step comprises an evaporation step for evaporating precursors of the elements necessary for formation of the film (2) and forming an evaporation area (16) with said elements, and in that said gas-treatment step comprises a step of ultrasound expansion of the flow (13) of gas delivered.

2. The method according to Claim 1, characterized in that the deposition step is a vacuum deposition step.

3. The method according to Claim 1 or Claim 2, characterized in that the gas-treatment step is performed before, after, or during the deposition step.

4. The method according to any one of Claims 1 to 3, characterized in that the gas-treatment step is a step of oxygenation, the flow (13) of gas being a flow of oxygen.

5. The method according to any one of Claims 1 to 3, characterized in that the gas-treatment step is a reducing step performed with forming gas, for example an argon/hydrogen mixture.

6. The method according to any one of the preceding claims, characterized in that the step of ultrasound expansion is performed via at least one ultrasound-expansion nozzle (26), through which the flow (13) of gas is delivered, said nozzle

being designed to generate a delivery area (40), in which at least as far as a distance of approximately 5 mm or approximately 10 mm from the nozzle there is an oxygen pressure approximately ten times the oxygen pressure outside the delivery area.

7. The method according to the preceding claim, characterized in that said nozzle (26) has a ratio between the inlet cross section and the outlet cross section comprised between approximately 1:2 and approximately 1:20.

8. The method according to any one of the preceding claims, characterized in that the gas-treatment step is performed cyclically.

9. The method according to any one of the preceding claims, characterized in that the deposition step and the gas-treatment step are performed in a vacuum chamber (6), and the step of treatment comprises a step of pressurization of the flow (13) of gas prior to said step of ultrasound expansion.

10. The method according to the preceding claim, characterized in that, in the deposition step, the substrate (4) is carried through an evaporation area (16) formed within the chamber (6).

11. The method according to the preceding claim, characterized in that the substrate (4) is tape-shaped and is fed continuously through the evaporation area (16).

12. The method according to Claim 10 or Claim 11, characterized in that the substrate (4) traverses the evaporation area (16) along a substantially curved path and the evaporation area (16) is radially internal to said path.

13. An apparatus (1) for deposition of films of coating

materials on a substrate, in particular for deposition of films of superconductive oxides and/or buffer layers of superconductive composite tapes, comprising a chamber (6), inside which are housed deposition means (10) for forming a film (2) of coating material on a face (11) of the substrate (4) and gas-treatment means (12) for delivering a flow (13) of gas on a working surface (14) of the substrate or of the film growing on the substrate, the apparatus being characterized in that the deposition means (10) comprise evaporation means (15) for evaporating precursors of the elements necessary for formation of the film (2) and forming an evaporation area (16) with said elements, and in that the gas-treatment means (12) comprise at least one ultrasound-expansion nozzle (26), through which said flow (13) of gas is delivered while undergoing ultrasound expansion.

14. The apparatus according to Claim 13, characterized in that said chamber (6) is a vacuum chamber.

15. The apparatus according to Claim 13 or Claim 14, characterized in that said nozzle (26) is designed to generate a delivery area (40), in which at least as far as a distance of approximately 5 mm from the nozzle there is an oxygen pressure approximately at least ten times the oxygen pressure in the chamber (6).

16. The apparatus according to Claim 15, characterized in that said nozzle (26) has a ratio between the inlet cross section and the outlet cross section comprised between approximately 1:2 and approximately 1:20.

17. The apparatus according to Claim 17, characterized in that the gas-treatment means (12) comprise at least one diffuser (25) provided with a plurality of ultrasound-expansion nozzles (26), and moving means (27) for bringing said diffuser (25) cyclically within the evaporation area (16).

18. The apparatus according to Claim 17 or Claim 18, characterized in that it comprises pressurization means (28) for feeding gas under pressure to said gas-treatment means (12).

19. The apparatus according to any one of Claims 17 to 19, characterized in that it comprises feed means (17) for carrying the substrate (4) through the evaporation area (16).

20. The apparatus according to Claim 20, characterized in that the substrate (4) is tape-shaped, and the feed means (17) are continuous-feed means for feeding the substrate through the evaporation area (16) continuously.

21. The apparatus according to Claim 20 or Claim 21, characterized in that the feed means (17) define a substantially curved path of the substrate (4) through the evaporation area (16), and the evaporation means (15) are set radially internal to said path.